Concentrations of polycyclic aromatic hydrocarbons (PAHs) and azaarenes in runoff from coal-tar- and asphalt-sealcoated pavement

Barbara J. Mahler [a,*], Peter C. Van Metre [a], William T. Foreman [b]

[a] U.S. Geological Survey, 1505 Ferguson Lane, Austin, TX 78754, USA
[b] U.S. Geological Survey National Water Quality Laboratory, Box 25046, Denver Federal Center, Denver, CO 80225, USA

ABSTRACT

Coal-tar-based sealcoat, used extensively on parking lots and driveways in North America, is a potent source of PAHs. We investigated how concentrations and assemblages of PAHs and azaarenes in runoff from pavement newly sealed with coal-tar-based (CT) or asphalt-based (AS) sealcoat changed over time. Samples of simulated runoff were collected from pavement 5 h to 111 d following application of AS or CT sealcoat. Concentrations of the sum of 16 PAHs (median concentrations of 328 and 35 μg/L for CT and AS runoff, respectively) in runoff varied relatively little, but rapid decreases in concentrations of azaarenes and low molecular weight PAHs were offset by increases in high molecular weight PAHs. The results demonstrate that runoff from CT-sealcoated pavement, in particular, continues to contain elevated concentrations of PAHs long after a 24-h curing time, with implications for the fate, transport, and ecotoxicological effects of contaminants in runoff from CT-sealcoated pavement.

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1. Introduction

Coal-tar-based (CT) pavement sealcoat, a potent source of polycyclic aromatic hydrocarbons (PAHs) (as reviewed in Mahler et al., 2012), is used extensively on asphalt pavement in many parts of the US and Canada. Fish kills have been reported when rainfall has resulted in runoff within hours after CT sealcoat application (RiverFox911, 2010; Hamilton County, 2011), and industry best-management practices recommend that CT sealcoat not be applied if rain is forecast within 24 hours (h), to allow the product time to cure (Construction Pros, 2013). Several questions thus arise: Should rainfall occur unexpectedly within 24 h of sealcoat application, what chemicals are present in runoff, and at what concentrations? If runoff occurs more than 24 h after application, how do chemical concentrations change during the following days, weeks, or months? And finally, how do chemical concentrations in runoff from CT-sealed pavement compare to those from pavement treated with an asphalt-based (AS) sealcoat product?

Sealcoat is a black, viscous liquid that is applied to the asphalt pavement of many parking lots, residential driveways, and even some playgrounds, although it rarely is used on roads. Sealcoat is marketed as protecting and beautifying the underlying asphalt. The two principal sealcoat formulations are asphalt-based and coal-tar-based. AS sealcoat primarily is used west of the Continental Divide, and typically contains about 50 mg/kg PAHs, although the concentration varies widely (4–8000 mg/kg for 11 products tested (City of Austin, 2005)). CT sealcoat primarily is used east of the Continental Divide and in parts of Canada (Diamond Environmental Group, 2011). CT sealcoat typically is 20–35% coal tar or coal-tar pitch, which are known human carcinogens; CT sealcoat products typically contain about 70,000 mg/kg PAH (Mahler et al., 2005), although, as with AS sealcoat, the concentration varies widely by product and manufacturer (6000 to 230,000 mg/kg for 14 products tested (City of Austin, 2005)).

Three previous studies have noted high concentrations of PAHs in runoff from pavement with CT sealcoat and changes with time following sealcoat application. The U.S. Geological Survey (USGS) measured concentrations of 12 aqueous-phase (filtered at 0.5 μm) and particle-associated PAHs in runoff from two CT-sealed pavement test plots and one AS-sealed pavement test plot beginning 15 days (d) after application (Mahler et al., 2004). The sum of concentrations of the PAHs measured, converted to whole-water (unfiltered) concentrations, in runoff from the CT-sealed pavement decreased from 48–64 (time [t] = 15 d) to 5–10 μg/L (t = 52 d); concentrations in runoff from the AS-sealed pavement decreased from 5.1 to 1.5 μg/L during the same period. More recently, the U.S. Environmental Protection Agency (EPA) measured PAHs in unfiltered runoff from CT-sealed pavement in a bench-scale study and in a field study (sealed pavement test plot with no

* Corresponding author.
E-mail addresses: bjmahler@usgs.gov (B.J. Mahler), pcvanmet@usgs.gov (P.C. Van Metre), wforeman@usgs.gov (W.T. Foreman).

vehicle traffic) (Rowe and O'Connor, 2011). In the bench-scale study, the sum of 17 PAHs measured decreased from more than 100 μg/L at $t = 24$ h (the manufacturer-recommended curing time) to about 10 μg/L ($t = 30$ d). The sum of the concentrations of the 17 PAHs in runoff from the test plot decreased from about 250 μg/L ($t = 24$ h) to about 80 μg/L ($t = 30$ d), but 160 d after application was still about 100 μg/L. One potentially important factor in both studies is that the test plots (or bench study) did not have vehicle traffic; yields of PAHs in runoff from in-use parking lots were reported to be significantly greater than from test plots because of abrasion of the dried sealcoat by vehicle tires (Mahler et al., 2005). In contrast, Watts et al. (2010) investigated PAH concentrations in runoff from two in-use parking lots, each commercially sealed with a different CT sealcoat product. The sum of concentrations of 16 PAHs in unfiltered runoff decreased from 5890 and 642 μg/L ($t = 26$ h) to 24 and 88 μg/L ($t = 18$ d), respectively. These studies added to our understanding of concentrations in PAHs in runoff from sealed pavement, but each had limitations. Mahler et al. (2004) reported concentrations of 54 PAHs and alkylated homologues, but samples were not collected until 15 d following application and the pavement had no vehicle traffic. Rowe and O'Connor (2011) collected samples beginning 24 h after application, but concentrations of individual PAHs were presented only in graphical form on a logarithmic scale, and the pavement had no vehicle traffic. Watts et al. (2010) collected samples beginning 26 h after application to pavement with vehicle traffic, but concentrations of individual PAHs were presented only in graphical form on a logarithmic scale, and AS-sealed pavement was not sampled.

An important question thus remains unanswered: How do PAH assemblages change in the hours to days following application of CT- and AS-sealant in a realistic setting (i.e., in-use pavement)? This is a key question from an environmental standpoint, as the low molecular weight (LMW) PAHs have different chemical characteristics and ecotoxicological properties than do the high molecular weight (HMW) PAHs (Eisler, 1987). Further, published studies have focused on PAHs, but coal tar contains many other chemicals, including azaarenes, a sub-class of heterocyclic aromatic compounds in which a nitrogen atom replaces a carbon atom in one of the aromatic rings of a PAH. Anthropogenic sources of azaarenes in the environment include coal-tar and oil-shale processing operations, wood-preserving facilities, and chemical manufacturing plants (de Voogt and Laane, 2009). Azaarenes include such compounds as quinolone, acridine, and carbazole; coal tar typically is about 1.5% (15,000 mg/kg) carbazole (Obloj-Muzaj et al., 1996). Several heterocyclic aromatic compounds, including azaarenes, have a large range of ecotoxicological effects, including acute toxicity, developmental and reproductive toxicity, cytotoxicity, photo-induced toxicity, mutagenicity, and carcinogenicity (Peddinghaus et al., 2012). The effects of azaarenes on organisms, however, are much less well studied than are those of PAHs (de Voogt and Laane, 2009).

Here we report concentrations of selected PAHs and three related heterocyclic compounds in the solid phase (scrapings of dried sealcoat) and PAHs and azaarenes in whole-water (unfiltered) runoff from parking lot pavement with CT sealcoat and with AS sealcoat. Sample collection began 5 h following sealcoat application and continued at increasing intervals to 36 d (AS sealcoat) or 111 d (CT sealcoat) following sealcoat application and subsequent vehicular use of the treated pavement.

2. Methods

2.1. Study site and sample collection

Samples were collected from two pavement test plots in areas of active use for parking and driving on the Pickle Research Campus, University of Texas at Austin (Supplementary material Fig. S1). The test plots are located about 630 m apart, and are separated by several intervening buildings and parking lots, precluding the possibility of aerial cross-contamination. A commercial applicator applied CT sealcoat (Tarconite, Neyra Industries, Inc.) to the first test plot at 11 am, August 23, 2011, and AS sealcoat (Paveshield, Neyra Industries, Inc.) to the second test plot at 11 am, September 20, 2011 (time of application, $t = 0$) (Material Safety Data Sheets provided in Supplementary material). Following a 24-h curing period the test plots were opened to normal traffic and parking activities.

Prior to sealcoat application, several 5-cm-diameter aluminum disks were placed on each test plot. One disk was removed from each test plot at 5 h and at 1, 3, 7, and 36 d following sealcoat application. A solid-phase sample was obtained by scraping dried sealcoat from the disk with a cleaned metal paint scraper.

Water used to simulate rain-water runoff was prepared at the USGS Columbia Environmental Research Center (CERC), Columbia, MO. The water was prepared as a mixture of CERC well water and deionized water and had the following water-quality characteristics: hardness of about 100 mg/L as $CaCO_3$, alkalinity of about 90 mg/L as $CaCO_3$, a pH of about 8.3, and the following concentrations of selected major ions and dissolved organic carbon (mg/L): Ca^{2+} 28, Mg^{2+} 10, K^+ 1.0, Na^- 10, Cl^- 12, SO_4^{2-} 19, and dissolved organic carbon 0.5 (Chris Ingersoll, written comm., USGS, 2011).

Runoff samples were collected beginning 5 h after application and sample collection continued at increasing intervals following the approach described by Mahler et al. (2005). All samples except the second were collected during the afternoon; the second sample was collected at 11:00 pm ($t = 12$ h). One sample of runoff from unsealed asphalt pavement was collected (unsealed control). For each sample, a 10 m^2 section of test plot was sprinkled with 25 L of the prepared water to simulate a light rain [25 mm (about 0.1 in)]. Runoff was collected with a peristaltic pump at the down-slope end of the pavement where the runoff pooled behind spill berms. Recovered water was split, while churning, into several 1-L baked amber glass bottles for analysis of PAHs and azaarenes and of suspended sediment concentration (SSC), and for archival purposes (frozen). Each subsequent runoff sample was collected from a new section of the test plot. Between August 1 and November 5, 2011, measurable rainfall occurred only on Oct 9 and 10 (112 and 38 mm, respectively) (Supplementary material Fig. S2), so the simulated runoff samples collected during at least the first 7 d following application represent runoff from the first "rainfall" to occur at an increasing length of time following sealant application.

2.2. Analytical

PAHs and heterocyclic compounds in solid-phase samples and in whole (unfiltered) water were analyzed at the USGS National Water Quality Laboratory (NWQL) in Lakewood, CO. Solid-phase samples for measurement of the 16 USEPA Priority Pollutant PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene), and three related heterocyclic compounds (9,10-anthraquinone, carbazole, and dibenzothiophene) were prepared and analyzed by gas chromatography/mass spectrometry using electron-impact ionization (GC/EIMS) according to Zaugg et al. (2006). Samples were analyzed in either the full-scan mode or selected ion monitoring mode.

The 16 USEPA Priority Pollutant PAHs and 7 azaarenes (quinoline, isoquinoline, acridine, phenanthridine, carbazole, benzo[c]cinnoline, and 2,2′-biquinoline) were measured in whole water. The 1-L unfiltered water samples were extracted and analyzed using procedures comparable to those described in Zaugg et al. (2007). In brief, upon arrival at the laboratory, the samples were treated with 60 g NaCl and then stored at 4 °C for as much as 14 d until extraction. Samples were fortified with surrogate compounds 2-fluorobiphenyl and p-terphenyl-d$_{14}$, and transferred to continuous liquid–liquid extractors (CLLE) with one rinse of the sample bottle with distilled water and two rinses with dichloromethane (DCM). Samples were extracted with DCM at ambient pH for 3 h, and then at pH 2 (by addition of 3 mL of a 25% H_2SO_4 solution) for an additional 3 h. The DCM extracts were concentrated by distillation within the CLLE. The extracts were further reduced to a final volume of 400 μL using N_2, followed by the addition of 20 μL of a 100-ng/μL procedural internal standard solution that includes 5 perdeuterated PAHs. The extracts were stored at ≤ -10 °C until analysis by GC/EIMS.

Because of anticipated high PAH concentrations in CT-runoff samples, only 1:10 and 1:100 dilutions of those extracts were analyzed. Reporting levels were raised accordingly. Undiluted extracts were analyzed for AS-runoff samples, with 1:10 dilution of extracts used for those analytes that exceeded the calibration curve in undiluted extracts. Reporting levels were based on method detection limits (MDLs) established using spiked reagent water or from instrument calibration quantitation limits for compounds without an MDL. Total PAH is reported as the sum of the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs (ΣPAH_{16}); non-detections were conservatively treated as zeroes for summation purposes. Pearson's correlation coefficient (r) and the coefficient of determination (r^2), where cited, are significant at $p < 0.05$.

Concentrations of suspended sediment were determined at the USGS Sediment Laboratory at the Louisiana Water Science Center. Samples were analyzed by filtration as described by Guy (1969).

2.3. Quality control

Quality assurance was provided by analyzing a field equipment blank (whole-water runoff), laboratory blanks, and spiked reagent samples, and by monitoring

recovery of surrogate compounds. Analytes in the field equipment blank either were not detected or were measured at estimated concentrations from 2 (fluorene) to 15 (carbazole) percent of the lowest environmental concentration measured for that analyte (Supplementary material Table S1). Analytes in laboratory blanks for the solid phase either were not detected or were measured at concentrations from 0.001 (benzo[b]fluoranthene) to 0.006 (acenaphthene) percent of the lowest environmental concentration measured for that analyte (data not shown). Analytes in laboratory blanks for whole water either were not detected or were measured at concentrations ranging from 0.01 (fluoranthene) to 2.6 (benzo[ghi]perylene) percent of the lowest environmental concentration measured for that analyte (data not shown). All spike recoveries were within NWQL established limits. A typical surrogate recovery range of 52–101% was observed for 2-fluorobiphenyl, but recoveries of p-terphenyl-d$_{14}$ (24–60%) were lower than typical in both CT- and AS-runoff samples, which might indicate that there was a matrix effect on the recovery of some of the HMW PAHs. Concentrations in runoff samples were not corrected for recovery of surrogates. Relative standard deviations were determined on the basis of laboratory set spike replicates ($n = 5$ for whole water and $n = 94$ for solid phase).

3. Results

3.1. Solid phase (dried sealcoat)

Concentrations of ΣPAH_{16} in dried CT sealcoat decreased from 93,300 mg/kg on the day of application to 46,300 mg/kg at $t = 36$ d, a decrease of 50% (Table 1; Supplemental material Table S2). During this period, there generally was a greater loss to the environment of LMW PAHs (2- and 3-ring) (median loss among compounds 84%) than of HMW PAHs (4-, 5-, and 6-ring) (median loss 36%). The PAH assemblage evolved from one dominated by phenanthrene to one dominated by fluoranthene (Fig. 1); fractional concentrations of most LMW PAHs decreased and those of most HMW PAHs increased, as observed by Van Metre et al. (2012) and attributed primarily to loss by volatilization. Losses of the heterocyclic
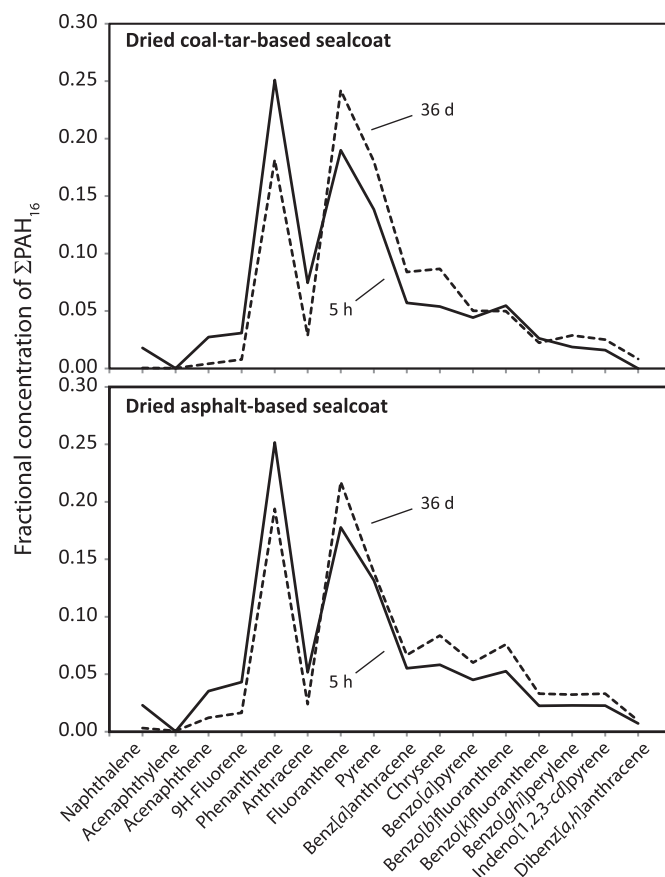

Fig. 1. Assemblage of the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs in scrapings of dried sealcoat collected 5 h and 36 d following sealcoat application to asphalt pavement test plots. Pearson's correlation coefficient (r) of 0.993 for the coal-tar-based sealcoat and asphalt-based sealcoat assemblages 5 h after sealcoat application.

compounds carbazole and dibenzothiophene (58 and 70%, respectively) were less than those of fluorene (88%), the PAH most similar to them in structure. Concentrations of 9,10-anthraquinone, an oxy-PAH formed by photo-induced oxidation of anthracene (Mallakin et al., 1999), increased by about 400% during the 36 d following sealcoat application.

Concentrations of ΣPAH_{16} in samples of dried AS sealcoat decreased from 6300 to 3500 mg/kg over the 36 d following application, a decrease of 45% (Tables 1,2). The initial concentration ($t = 5$ h) of 6300 mg/kg was at the upper end of the range measured by the City of Austin for 11 asphalt-based products (4 mg/kg to 8000 mg/kg) (City of Austin, 2005). The PAH assemblage of the initial sample of dried AS sealcoat was very similar to that of the dried CT sealcoat (Fig. 1) (r of 0.993; dibenz[a,h]anthracene not included in the correlation as it was not detected in any sample). Over the 36 d that followed application, the dried AS sealcoat had large losses of LMW PAHs, smaller losses of HMW PAHs, and a large increase in 9,10-anthraquinone concentration, similar to changes measured for dried CT sealcoat (Table 1). The relatively high PAH concentrations in the dried AS-sealcoat and the similarity of its PAH assemblage to that of dried CT sealcoat indicates that the AS sealcoat applied might have contained some CT sealcoat. Assuming a PAH concentration in "pure" AS sealcoat of 50 mg/L, an addition of 7% CT sealcoat (containing a PAH concentration of 93,000 mg/kg) would be sufficient to explain a concentration of 6300 mg/kg in the AS sealcoat applied.

Table 1
PAH loss over the first 36 days following sealcoat application. A negative value indicates a loss, a positive value indicates a gain. Concentrations for individual PAHs provided in Table S1. [NC, not computed because at least one value was a non-detection; ΣPAH_{16}, sum of the 16 USEPA Priority Pollutant PAHs; NM, not measured].

Compound	Change over 36 d (%)			
	Scrapings		Runoff	
	Coal-tar-sealcoated pavement	Asphalt-seacoated pavement	Coal-tar-sealcoated pavement	Asphalt-sealcoated pavement
Polycyclic aromatic hydrocarbon				
Naphthalene	−99%	−92%	−98%	−80%
Acenaphthylene	−11%	26%	NC	NC
Acenaphthene	−92%	−81%	−96%	−94%
Fluorene	−88%	−79%	−93%	−27%
Phenanthrene	−64%	−58%	−71%	−89%
Anthracene	−81%	−75%	−89%	−70%
Fluoranthene	−37%	−33%	49%	341%
Pyrene	−35%	−42%	51%	286%
Benz[a]anthracene	−27%	−34%	50%	514%
Chrysene	−20%	−21%	203%	763%
Benzo[b]fluoranthene	−55%	−21%	242%	853%
Benzo[k]fluoranthene	−58%	−20%	201%	1154%
Benzo[a]pyrene	−44%	−27%	195%	897%
Indeno(1,2,3-cd)pyrene	−22%	−20%	272%	1734%
Dibenz[a,h]anthracene	NC	−27%	NC	NC
Benzo[ghi]perylene	−24%	−23%	288%	2400%
ΣPAH_{16}	−50%	−45%	15%	63%
Heterocyclic compound				
Quinoline	NM	NM	−92%	NC
Isoquinoline	NM	NM	−95%	NC
Acridine	NM	NM	−76%	−38%
Phenanthridine	NM	NM	−42%	−55%
Carbazole	−58%	−24%	−92%	−76%
Dibenzothiophene	−70%	−50%	NM	NM
9,10-Anthraquinone	405%	212%	NM	NM

Table 2
Sums of the concentrations of the 16 USEPA Priority Pollutant PAHs (ΣPAH_{16}), of the low molecular weight PAHs (2- and 3-rings; ΣPAH_{LMW}), and the high molecular weight PAHs (4-, 5, and 6-rings; ΣPAH_{HMW}) in samples of simulated runoff, in micrograms per liter.

Surface type	Sample date	Time after sealcoat application (hours)	Time after sealcoat application (days)	Suspended sediment concentration (mg/L)	ΣPAH_{16}	ΣPAH_{LMW}	ΣPAH_{HMW}
Coal-tar sealcoat	23-Aug-2011	5	0.2	8	357	220	136
	23-Aug-2011	12	0.5	1	237	130	107
	24-Aug-2011	26	1	5	343	233	110
	25-Aug-2011	54	2	10	190	107	84
	26-Aug-2011	75	3	13	202	92	109
	30-Aug-2011	173	7	35	476	98	378
	28-Sep-2011	866	36	48	409	55	354
	26-Oct-2011	1541	64	30	167	21	145
	12-Dec-2011	2666	111	31	328	45	283
Asphalt sealcoat	20-Sep-2011	4	0.2	9	38	30	8
	20-Sep-2011	11	0.5	5	21	16	5
	21-Sep-2011	26	1	9	35	27	8
	22-Sep-2011	50	2	14	43	34	9
	23-Sep-2011	74	3	15	33	24	9
	27-Sep-2011	170	7	37	27	17	10
	26-Oct-2011	865	36	104	63	12	50
Unsealed asphalt	27-Sep-2011	n/a	n/a	598	17	1.4	16

3.2. Aqueous phase (unfiltered runoff)

Runoff samples did not indicate any physical fouling. Runoff samples were clear with an amber hue (Supplementary material Fig. S3), and samples collected in the hours to days following sealcoat application contained low concentrations (≤ 10 mg/L) of suspended sediment (Table 2).

Fourteen of the 16 PAHs were detected in all runoff samples from the CT- and AS-sealed test plots; the exceptions were acenaphthylene and dibenz[a,h]anthracene (Supplementary material Table S1). Four of the 16 PAHs were not detected in the control sample (runoff from unsealed asphalt): three 3-ring PAHs (acenaphthene, acenaphthylene, and fluorene) and dibenz[a,h]anthracene. The median concentration of ΣPAH_{16} in the CT-sealed runoff (328 μg/L) was about 19 times higher than the concentration in the unsealed asphalt control (17 μg/L); the median concentration in the AS-sealed runoff (35 μg/L) was about twice as high as the concentration in the control (Table 2).

Overall, concentrations of ΣPAH_{16} in runoff samples varied within a factor of about 3, but did not systematically increase or decrease. At the end of the sampling period, concentrations of ΣPAH_{16} were similar to those in the initial sample (CT) or greater than those in the initial sample (AS) (Fig. 2). In contrast, concentrations of individual PAHs varied substantially: concentrations of most LMW PAHs decreased by about an order of magnitude, and concentrations of most HMW PAHs increased by a factor of 2–4 (Supplementary material Table S1). Similar to the solid-phase samples, ΣPAH_{16} in the initial runoff sample was dominated by phenanthrene for both CT-sealed (131 μg/L) and AS-sealed (13.0 μg/L) test plots, and in the final sample was dominated by fluoranthene (CT runoff 70.4 μg/L; AS runoff 14.2 μg/L) (Supplementary material Table S1). The sum of the concentrations of the LMW PAHs (ΣPAH_{LMW}) for CT runoff, which initially was greater than the sum of the HMW PAHs (ΣPAH_{HMW}), decreased to about 26% of ΣPAH_{HMW} by $t = 7$ d (Table 2), and the ratio of ΣPAH_{LMW} to ΣPAH_{HMW} remained relatively constant during $t = 7-111$ d (Fig. 3a). ΣPAH_{LMW} from both test-plot types generally decreased over the sampling period, with the exception of anomalously low concentrations in the second sample collected (the only nighttime sample; $t = 12$ h), whereas ΣPAH_{HMW} decreased slightly over the first 2 days then generally increased but was variable (Fig. 3b and c). The SSC also generally increased, ranging from less than 10 mg/L (both CT and AS) in the initial sample to 31 mg/L in the final CT sample and

104 mg/L in the final AS sample (Table 2). ΣPAH_{HMW} was positively related to SSC for both CT runoff ($r^2 = 0.75$) and AS runoff ($r^2 = 0.94$). [SSC and ΣPAH_{LMW} were inversely related for CT runoff ($r^2 = 0.50$) but not significantly related for AS runoff. SSC and ΣPAH_{16} were positively related for both CT runoff ($r^2 = 0.62$) and AS runoff ($r^2 = 0.60$).] The strong relation between SSC and ΣPAH_{HMW} likely is because much of the SSC consisted of abraded sealcoat particles.

Of the seven azaarenes measured, acridine, phenanthridine, and carbazole were detected in every runoff sample, including the unsealed runoff control (Supplementary material Table S1). Quinoline and isoquinoline were detected in all samples of CT and most samples of AS runoff but not in the control, and benzo[c]cinnoline and 2,2'-biquinoline were not detected in any samples. Concentrations of carbazole were consistently much higher than those of the other azaarenes; in the initial CT sample, the concentration of carbazole (750 μg/L) also exceeded that of any of the 16 PAHs by a factor of 5 or more. Concentrations of the azaarenes in runoff generally decreased following sealcoat application. For all azaarenes measured, the concentration in the sample collected at night
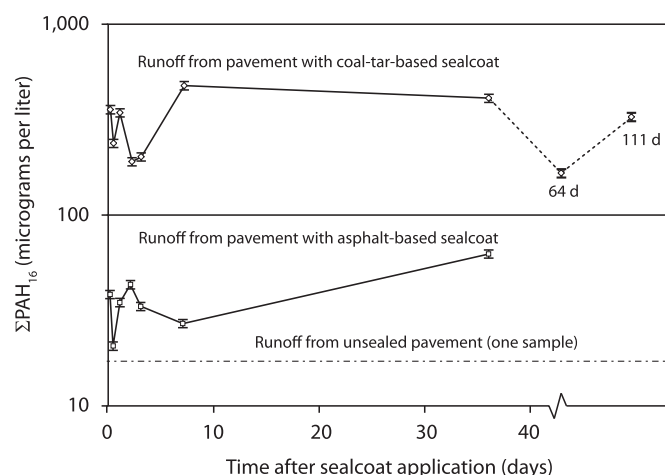

Fig. 2. The sum of concentrations of the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs (ΣPAH_{16}) in runoff following application of sealcoat to asphalt pavement test plots. Error bars indicate relative standard deviation determined on the basis of laboratory replicates.
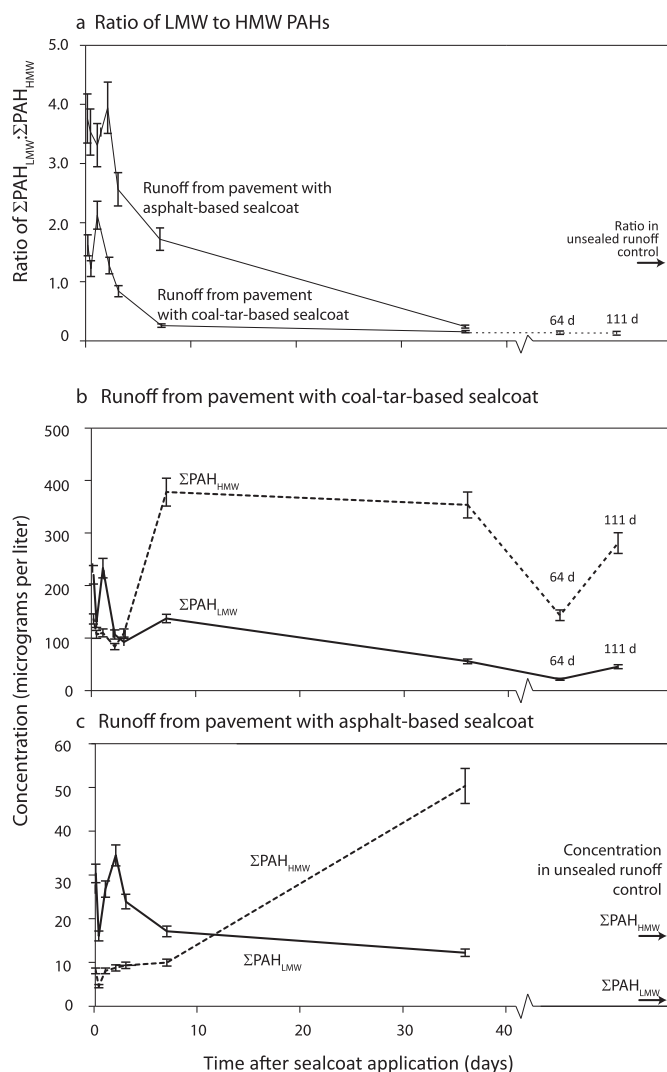
Fig. 3. (a) Time-series of the ratio of the sum of concentrations of the low molecular weight (2- and 3-ring) PAHs (ΣPAH_{LMW}) to that of the high molecular weight (4-, 5-, and 6-ring) PAHs (ΣPAH_{HMW}) in runoff following application of sealcoat to asphalt pavement test plots. (b) Changes in ΣPAH_{LMW} and ΣPAH_{HMW} in runoff following application of coal-tar-based sealcoat. (c) Changes in ΣPAH_{LMW} and ΣPAH_{HMW} in runoff following application of asphalt-based sealcoat. Error bars indicate relative standard deviation determined on the basis of laboratory replicates.

($t = 12$ h) was lower than in the preceding and following samples, and for several compounds (quinoline, isoquinoline, acridine, and phenanthridine in CT runoff and quinoline in AS runoff) the concentration in the sample collected 7 d after application was higher than in the preceding or following sample (Supplementary material Table S1), possibly related to the increase in SSC between 3 and 7 d following application. Even in the final sample collected, concentrations of the azaarenes in runoff, when detected, exceeded those in the control sample by a factor of 7–36 (CT runoff) or 3–10 (AS runoff) (Supplementary material Table S1).

4. Discussion

A primary objective of this study was to compare the chemistry of runoff from CT- and AS-sealed pavement. The chemical composition of the dried AS-sealcoat product and the runoff from the AS-sealed test plot indicates that the product might have contained some coal-tar pitch, equivalent to about 7% CT sealcoat. Some mixing might occur as an applicator switches from one type of

sealcoat to another, although the applicator stated that the tank and other equipment used had been cleaned before filling the tank with AS sealcoat (Marcia Pederson, Stripe-Rite, oral communication, 2013). The mixing of some CT sealcoat with AS sealcoat also might have occurred at some point in the supply chain. Similar anomalous findings have been reported by the City of Austin: of 11 AS-sealcoat products analyzed, 2 had much higher concentrations (about 1500 and 8000 mg/kg) than the other 9, although much lower than those in most CT-sealcoat products analyzed (median concentration ~ 70,000) (City of Austin, 2005). The two AS-sealcoat products with high concentrations were among five obtained from commercial distributors who provide products to applicators; six retail (off-the-shelf) products all had low PAH concentrations. We conclude that it might not be uncommon for sealcoat marketed as AS sealcoat to contain a small amount of CT sealcoat, which can increase PAH concentrations in the AS sealcoat by one or more orders of magnitude. The concentrations measured here for the AS test plot likely represent a high-end concentration scenario for runoff from AS-sealed pavement, but little information on quality control involved in AS sealcoat production and distribution is available.

Concentrations of ΣPAH_{16} concentrations in runoff from CT-sealed pavement, and, to a lesser degree, AS-sealed pavement remained high long after a 24- or even 48-h curing time had passed (Fig. 2, Table 2). This indicates that deleterious effects of runoff from CT-sealed pavement, and, to a lesser extent, AS-sealed pavement to aquatic organisms might continue for days to even months after application. For example, the LC50 (the concentration at which 50% of the population will die) for rainbow trout (*Oncorrhynchus mykiss*) exposed to phenanthrene was reported as 30 μg/L (Milleman et al., 1984); this concentration was exceeded in every sample of CT-sealcoat runoff collected during the 7 d following application. Rainbow trout exposed to water containing sand contaminated with benzo[*a*]pyrene at a concentration of 0.2 μg/L resulted in gross anomalies in 6.8% of the population (Hose et al., 1984); this concentration in CT-sealcoat runoff was exceeded by a factor of 10 in runoff collected during the first 7 d after application and by a factor of 100 in most runoff samples collected from 7 to 111 d after application; it also was exceeded by as much as a factor of 10 in one of the AS-sealcoat runoff samples. Toxicity might be exacerbated for organisms exposed to sunlight; some PAHs adsorb UV light, which alters the reactivity of the PAH and can render it more toxic, although these effects pertain primarily to aquatic species in shallow water (Meador, 2010). For example, bluegill sunfish (*Lepomis macrochirus*) exposed to anthracene at a concentration of 12.7 μg/L died within 48 h when they were in bright sunlight (Bowling et al., 1983). This concentration was exceeded in all but one of the CT runoff samples collected during the 7 d following application; it was not exceeded in any of the AS runoff samples.

The concentrations measured here are substantially higher than those reported by Mahler et al. (2004) and, to a lesser extent, by Rowe and O'Connor (2011). This difference might arise for one or more reasons. First, Mahler et al. reported only the concentration of the sum of the 12 parent PAH (ΣPAH_{12}); when ΣPAH_{12} is computed for the data presented here, however, the concentration is only 10–30% less than the concentration of ΣPAH_{16}, insufficient to account for the much larger difference in concentrations between the two studies. (Seventeen PAHs were analyzed by Rowe and O'Connor). Second, although the same brand of CT and AS sealcoat was applied for both the Mahler et al. (2004) study and the study presented here, the concentration of ΣPAH_{12} in scrapings of dried sealcoat ($t = 7$ d) for the current study was higher than that for the 2004 study ($t = 14$ d) by a factor of 6 for CT sealcoat (67,000 and 11,000 mg/kg, respectively) and a factor of 16 for AS sealcoat (1870 and 110 mg/kg, respectively). The difference in PAH concentration in the product therefore might account for the difference in

concentrations in the runoff. PAH concentrations in sealcoat product or scrapings were not reported by Rowe and O'Connor. Third, the test plots used in the Mahler et al. and Rowe and O'Connor studies did not have any vehicle traffic, eliminating the potential for abrasion of dried sealcoat by vehicle tires. Although Rowe and O'Connor reported an increase in SSC with time similar to that noted for this study, they reported a decrease rather than an increase in PAH concentrations, indicating that a source other than abraded sealcoat, such as windblown dust, might have been the source of the particles in the runoff.

Azaarene concentrations in runoff decreased over the days following sealcoat application. One compound, acridine, was present at a concentration associated with acute toxicity (LC50 for the midge *Chironomus riparius* [first instar larvae] of 71.4 μg/L (Bleeker et al., 1998)) in the first sample collected ($t = 5$ h) from CT-sealed pavement (Supplementary material Table S1). Concentrations of carbazole in runoff samples from CT-sealed pavement collected 5 h and 1 d following application were within a factor of 2 of the LC50 of 930 μg/L reported for zebrafish embryos (*Danio rerio*) (Peddinghaus et al., 2012). Concentrations of acridine and carbazole in initial runoff samples from AS-sealed pavement were an order of magnitude or more lower than those in runoff from CT-sealed pavement. Azaarones, products of photo-oxidation of azaarenes, generally are more toxic than the parent compound (de Voogt and Laane, 2009), but were not measured for this study.

The change in the PAH assemblage, from one dominated by LMW PAHs to one dominated by HMW PAHs, likely resulted from volatilization of the LMW PAHs from the dried sealcoat (Van Metre et al., 2012) and mobilization of HMW PAHs as the dried sealcoat began to abrade. The decrease in the concentration of LMW PAHs in runoff is consistent with the decrease in concentration of LMW PAHs in the solid phase over the 36 d following application (Supplementary material Table S2). Although photooxidation accounts for some loss of PAHs from the solid phase, it likely is a small fraction: for example, the increase in concentration of the oxy-PAH 9,10-anthraquinone in dried CT sealcoat scrapings from 112 to 566 mg/kg during the 36 d following application accounts for less than one-tenth of the decrease in anthracene concentration from 6940 to 1320 mg/kg (Supplementary material Table S2). The highest concentrations of LMW PAHs occurred in the earliest samples, which also had the lowest SSC (<10 mg/L). On the basis of estimates using Koc, during the first 2 d (CT) or first 3 d (AS) from 10 to 60% of the mass of LMW PAHs was in the aqueous phase (Supplementary material Table S3). The temporary decrease in ΣPAH_{16} in the second sample ($t = 12$ h) from both test plot types might have occurred for two reasons: (1) these samples had the lowest SSC (Table 2), translating to a lower total mass in the solid phase, and (2) they were collected at nighttime when the temperature of the pavement was lower. The solubility of PAHs (and azaarenes) increases with temperature; the median temperature of the pavement for the daytime samples collected during the first 7 d following sealcoat application was 62.1 °C, whereas the pavement temperature when the nighttime sample was collected was estimated to be about 39 °C. (Pavement temperature was not measured when the nighttime sample was collected in August (CT) or September (AS) 2011, but the temperature of recently sealed pavement measured at 10:15 pm September 3, 2013, was 39 °C). The time-series response of azaarene concentrations was similar to that of the LMW PAHs (Supplementary material Table S1), including the decrease in concentrations for the nighttime sample. Although azaarenes are relatively insoluble in cold water, they are readily soluble in hot water (Environment Canada, 2011). The contact of water with hot pavement therefore might increase leaching of PAHs and azaarenes from pavement sealcoat.

Concentrations of the HMW PAHs in runoff from both CT and AS test plots, in contrast to those of the LMW PAHs, generally increased following sealcoat application and are positively related to SSC. A regression of benzo[a]pyrene (BaP) with SSC, for example, has an r^2 of 0.84 (CT) or 0.95 (AS) and an intercept that is not significantly different from 0 (p-value for intercept > 0.05), indicating that BaP in the aqueous phase was negligible. This interpretation is supported by partitioning estimates based on Koc (Supplementary material Table S3). Regression slopes of 0.58 (CT) and 0.033 (AS) correspond to a BaP concentration associated with particles in runoff of 580 mg/kg and 33 mg/kg for CT and AS runoff, respectively. A BaP concentration of 580 mg/kg for particles in CT runoff is within the upper range of that measured on particles vacuumed from CT-sealed parking lots in Austin (21—671 mg/kg, median 285 mg/kg); a concentration of 33 mg/kg for particles in AS runoff exceeds those measured on particles vacuumed from AS-sealed parking lots by about 2 orders of magnitude (0.06—0.6 mg/kg, median 0.56 mg/kg) (Mahler et al., 2010). The increase in concentrations of HMW PAHs, then, corresponds to an increase in SSC as the sealcoat begins to wear and abraded sealcoat particles become entrained in runoff. SSC measured for this study was about twice as high as that measured by Rowe and O'Connor (2011) and 2 to 3 times higher than that measured by Mahler et al. (2004) at similar intervals after sealant application, indicating the effect of vehicle traffic on SSC, and, therefore, PAH concentration, loads, and yields. SSC measured here, however, was not as high as that measured in runoff from in-use sealed parking lots with sealant applied months to years earlier (Mahler et al., 2004). PAH concentrations and loads in runoff, therefore, might increase as sealcoat ages and is abraded by vehicles. Additionally, the higher intensity of natural storms might mobilize particles more aggressively than the simulated rainfall used here, and might therefore contribute to higher SSC and PAH concentrations.

The evolution of the chemical assemblage in runoff over the first 36 d following sealcoat application to one that contains predominantly particle-associated HMW PAHs has implications for the fate and transport of chemicals associated with runoff from sealed pavement. Chemicals in the aqueous phase will not be retained by stormwater ponds or other stormwater management structures, and therefore might contaminate downstream water bodies. The presence of aqueous-phase chemicals in receiving water bodies in response to runoff events, however, will be transient, as the chemicals are diluted, move downstream, or are degraded by photolysis or by microorganisms. Additionally, chemicals in the aqueous phase can leach into shallow groundwater, particularly in highly vulnerable aquifers such as karst, where there is a direct and rapid connection between surface water and groundwater. Concentrations of individual PAHs in uncontaminated groundwater usually are in the range of 0—5 ng/L, but at heavily contaminated sites exceed 10 μg/L (World Health Organization, 2003). Contamination of groundwater by azaarenes has been well documented for sites contaminated with coal-tar oils or creosote (International Agency for Research on Cancer, 1999; Hartnik et al., 2007; Reineke et al., 2007). In contrast, particle-associated HMW PAHs tend to collect in soils and in streambed and lake sediment, where, because of their persistence, they can remain for many years. For example, soil contaminated by PAHs from coal tar at old manufactured gas plants (MGPs) continues to present an expensive contamination problem decades after these plants were shut down (Hawthorne et al., 2002).

The decrease over time in concentrations of aqueous-phase LMW and the increase in concentrations of particle-associated HMW PAHs in sealcoat runoff has implications for ecotoxicology. LMW PAHs can be acutely toxic to aquatic organisms, whereas the HMW PAHs are appreciably less toxic than the LMW PAHs, but

many HMW PAHs are carcinogenic, mutagenic, or teratogenic to a wide variety of organisms, including fish, amphibians, birds, and mammals (Eisler, 1987). Azaarenes are more water soluble than PAHs and therefore are likely to be more bioavailable (Pearlman et al., 1984). The shift from aqueous-phase compounds to particle-associated compounds at about 7 d after CT sealcoat application therefore might correspond to a shift from acute toxicity to chronic toxicity and other ecotoxicological effects, such as cyto- and genotoxicity.

5. Conclusions and implications

Concentrations of PAHs in runoff from CT-sealed pavement remained high for weeks to months following sealcoat application, but the assemblage evolved to one predominantly composed of particle-associated HMW PAHs. This evolution might have important ecotoxicological implications, as LMW are acutely toxic and HMW are mutagenic, teratogenic, and carcinogenic. Elevated concentrations of aqueous-phase LMW PAHs and azaarenes during the first 7 d following application indicate a potential source of contamination to groundwater, and hot summer temperatures might increase leaching of these chemicals from the sealcoat. This study is the first, to our knowledge, to document elevated concentrations of azaarenes associated with use of CT sealcoat. Because of the extensive use of CT-sealcoat products in North America, azaarene contamination might be more widespread than previously considered. Finally, this study demonstrates that sealcoat products marketed as containing only asphalt might contain some CT sealcoat at up to several percent by weight, and might therefore contain PAHs at concentrations one to two orders of magnitude higher than a true asphalt-based product.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.01.008.

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